

# PATENT SPECIFICATION

NO DRAWINGS

L076.688

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Date of Application and filing Complete Specification: Dec. 8, 1965.

No. 52124/65.

Application made in Germany (No. F44637 IVd/39c) on Dec. 8, 1964.

Application made in Germany (No. F46918 IVd/39c) on Aug. 17, 1965.

Complete Specification Published: July 19, 1967.

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Index at acceptance:—C3 R(32C1, 32C4, 32C5, 32C6, 32C7, 32C8, 32C10, 32C11, 32C12, 32C16, 32D1, 32D4, 32D6C, 32D6D, 32E1, 32E2, 32E3, 32E4, 32E5, 32E6, 32E7, 32E8, 32E9, 32E10, 32F2, 32F3, 32F4, 32F5, 32FX, 32G2, 32J1, 32J2Y, 32J3, 32J4, 32J5, 32S)

Int. Cl.:—Co 8 g 21/04

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:— WOLFGANG KEBERLE, Bergisch-Neukirchen, Imbach 36 f, Germany, and DIETER DIETERICH, Leverkusen, Ludwig-Girtler-Strasse 1, Germany; both of German nationality.

## COMPLETE SPECIFICATION

### Polyurethane Resins

- We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate, organised under the Laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process for the production of polyurethane resins.
- The production of polyurethane resins having cationic groups to impart cationic properties thereto by incorporating into polyurethane compositions tertiary nitrogen atoms which can be quaternised is already known. The basicity and the cationic character of the resin is determined by its incompatibility with alkalis, alkaline substances, substances which split off bases and anionic synthetic resins. Polyurethanes containing ionic groups which are compatible to a large extent with alkalis, alkaline substances, substances which split off bases and especially with anionic polymer resins are therefore of particular interest.
- This invention relates to such anionic polyurethanes which owing to their unexpected properties and their versatility open up new fields of application for polyurethane resins.
- It is known that soluble polyureas which contain one acid group for every 400 to 500 molecular weight units can be prepared from diisocyanates and diamino-carboxylic acids and sulphonic acids or their salts. Such products are prepared in high boiling polar solvents such as N,N-dimethyl formamide and formamide and isolated by precipitation with acetone. In water, these anionic polyureas form molecular disperse, clear solutions which are highly viscous even at low concentrations such as 1% by weight, for example, and which dry to hard, brittle, gelatinous masses which can easily be redissolved in water. The products are insoluble in low boiling organic solvents such as acetone, ethyl methyl ketone, ethyl acetate, benzene and toluene and can be precipitated as pulverulent and crystalline precipitates from N,N-dimethylformamide or formamide solution by the said solvents. Owing to their great hydrophilicity and brittleness, no use has been found for them as synthetic resins.
- According to the invention, in contrast thereto, polyurethane resins are obtained which are built up in the manner of block anionic polymers the organic blocks of which are interrupted by short segments carrying salt-type groups or are terminated by segments carrying salt-type groups. In this way there are obtained synthetic resins which have a predominantly hydrophobic character but owing to the presence of the anionic salt-type groups they have hydrophilic centres which enable aqueous colloidal solutions or aqueous dispersions to be prepared from them. However, the hydrophilic properties are in no case so great that molecular disperse, pure aqueous solutions are produced. Surprisingly such anionic polyurethane block polymers have properties with which the technologist is familiar from vulcanised synthetic rubber, i.e. high strength, a slightly to highly elastic character, low permanent elongation, insolubility in water, resistance to hydrocarbons and numerous solvents.

No high-boiling or special polar solvents are required for preparing these synthetic resins. If desired, the usual commercially readily available solvents such as acetone, methyl ethyl ketone, ethyl acetate and alcohols may be used, if desired mixed with water. The products are then isolated by simply removing the solvent during a forming process.

The present invention accordingly provides a process for the preparation of polyurethane resins which comprises reacting together a predominantly linear compound having reactive hydrogen atoms and at least one hydroxyl group and a molecular weight of 300 to 20,000, a polyisocyanate if desired chain lengthening agents having reactive hydrogen atoms, and a compound having at least one hydrogen atom reactive with isocyanate groups and at least one anionic salt-type group or group capable of anionic salt formation. The ratio of isocyanate groups to hydrogen atoms reactive with isocyanate groups in the compounds capable of salt formation being such that the groups capable of salt formation present do not undergo reaction with the isocyanate groups, and the resulting polyurethane is subsequently converted at least partly to the salt form by reaction with an organic or inorganic base in the case where groups capable of salt formation are present, the proportion by weight of the salt type groups contained in the polyurethane being more than 1% and not more than 15% and, when the groups capable of salt formation are carboxyl groups, not more than 8%.

Compounds with several reactive hydrogen atoms suitable for the process of the invention are substantially linear and have a molecular weight of 300 to 20,000, preferably 500 to 4,000. These compounds which are known per se, have terminal hydroxyl- and carboxyl-, amino and/or mercapto groups; polyhydroxy compounds such as polyesters, polyacetals, polyethers, polythioethers, polyamides and polyester amides are preferred.

Suitable polyethers which may be mentioned are, for example, the polymerisation products of ethylene oxide, 1,2-propylene oxide, tetrahydrofuran, 1,4-butylene oxide and their copolymerisation or graft polymerisation products and the polyethers obtained by condensation of polyhydric alcohols or mixtures thereof and those obtained by alkoxylation of polyhydric alcohols, amines, polyamines and amino alcohols.

Suitable polyacetals are, for example, the compounds obtainable from 1,6-hexanediol and formaldehyde.

Polythioethers that are particularly useful are condensation products of thiodiglycol and its mixtures with other glycols or polyhydroxy compounds.

Suitable polyesters, polyester amides and polyamides include the predominantly linear condensates obtained from saturated and un-

saturated polybasic carboxylic acids and saturated and unsaturated polyhydric alcohols, amino alcohols, diamines, polyamines and mixtures thereof, and, for example, polyterephthalates and polycarbonates.

Polyhydroxy compounds which already contain urethane or urea groups as well as natural polyols which may be modified, e.g. castor oil and carbohydrates, may also be used.

The lyophilic or hydrophobic character and mechanical properties of the products of the process can be varied by using mixtures of different polyhydroxy compounds.

Suitable polyisocyanates include any aromatic and aliphatic diisocyanates such as 1:5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyldimethylmethane diisocyanate, di- and tetraalkyldiphenylmethane - 4,4' - diisocyanates, 4,4'-dibenzyl diisocyanate, 1:3 - phenylene-diisocyanate, 1:4 - phenylenediisocyanate, the isomers of toluylene diisocyanate, if desired in admixture, chlorinated and brominated diisocyanates, diisocyanates containing phosphorus, butane - 1:4 - diisocyanate, hexane-1:6 - diisocyanate, dicyclohexylmethane-4,4' - diisocyanate and cyclohexane - 1:4-diisocyanate.

Of particular interest are partially masked polyisocyanates which enable self-cross-linking polyurethanes to be formed, e.g. dimeric toluylene diisocyanate or polyisocyanates which have been partly reacted e.g. with phenol, tertiary butanol, phthalimide or caprolactum.

Chain lengthening agents having reactive hydrogen atoms include the following:

1. The usual saturated and unsaturated glycols such as ethylene glycol or condensates of ethylene glycol, 1,4 - butanediol propane-1:2 - diol, propane - 1:3 - diol, neopentyl glycol, 1,6 - hexanediol, isomers of bis-hydroxymethyl - cyclohexane, 4,4' - bis - ( $\beta$ -dihydroxyethyl) - diphenyldimethylmethane, mono- and bis-alkoxylated aliphatic, cycloaliphatic, aromatic and heterocyclic primary amines such as N-methyl-diethanolamine, N-butyl-diethanolamine, N:N-bis- $\gamma$ -aminopropyl-N-methylamine, N-oleyldiethanolamine, N - cyclohexyldiisopropanolamine, N:N - dihydroxyethyl - p - toluidine, N:N - dihydroxypropylnaphthylamine, polyethoxylated N-butyldiethanolamine polypropoxylated N-methyldiethanolamine (molecular weight 300-4000), polyesters having tertiary amino groups, and dimethyl - bis - hydroxyethyl-hydrazine;

2. Aliphatic, cycloaliphatic and aromatic diamines, such as ethylene diamine, hexamethylene diamine, 1:4 - cyclohexylenediamine, benzidine and 4,4' - diaminodiphenylmethane, the isomers of phenylene diamine, hydrazine, and ammonia;

3. Amino alcohols such as ethanolamine, propanolamine and butanolamine;

4. Aliphatic, cycloaliphatic, aromatic and

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- heterocyclic mono- and diaminocarboxylic acids, such as glycine,  $\alpha$ - and  $\beta$ -alanine, 6-aminocaproic acid, 4-aminobutyric acid, the isomeric mono- and diaminobenzoic acids and the isomeric mono- and diaminonaphthoic acids;
5. Water.
- Compounds which contain at least one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation which may be used, if desired in admixture, include the following, e.g.
1. Hydroxy- and mercapto acids such as glyceric acid, glycollic acid, thioglycollic acid, lactic acid, trichlorolactic acid, malic acid, dihydroxymaleic acid, dihydroxyfumaric acid, tartaric acid, dihydroxytartaric acid, mucic acid, saccharic acid, citric acid, glyceroboric acid, pentaerythritol-boric acid, mannito-boric acid, salicylic acid, 2:6 dihydroxybenzoic acid, protocatechuic acid,  $\alpha$ -resorcylic acid,  $\beta$ -resorcylic acid, hydroquinone - 2:5 - dicarboxylic acid, 4-hydroxyisophthalic acid, 4:6 dihydroxy-isophthalic acid, hydroxyterephthalic acid, 5:6:7:8 - tetrahydronaphthal - (2) - carboxylic acid - (3), 1-hydroxy - naphthoic acid - (2), 2:8 - hydroxynaphthoic acid - (3),  $\beta$  - hydroxypropionic acid, m-hydroxybenzoic acid, pyrazolone-carboxylic acid, uric acid, barbituric acid and 2:6 - bis - hydroxymethyl - p - cresol;
2. Aliphatic, cycloaliphatic, aromatic and heterocyclic mono- and diaminocarboxylic acids, such as glycine,  $\alpha$ - and  $\beta$ -alanine, 6-aminocaproic acid, 4-aminobutyric acid, the isomeric mono- and diaminobenzoic acids and the isomeric mono- and diaminonaphthoic acids;
3. Aliphatic, cycloaliphatic, aromatic and heterocyclic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, the isomeric phthalic acids, diphenic acid, the isomeric naphthalic acids, maleic acid, fumaric acid, sulphodiacytic acid, diglycollic acid, thiodiglycollic acid, methylene - bis - thioglycollic acid, the isomeric pyridine dicarboxylic acids, the isomeric quinoline dicarboxylic acids, ethylene diamino-tetraacetic acid and nitrile-triacetic acid;
4. Hydroxy- and carboxy-sulphonic acids: 2 - Hydroxyethanesulphonic acid, phenolsulphonic acid-(2), phenolsulphonic acid-(3), phenolsulphonic acid-(4), phenol - disulphonic acid-(2,4), sulphoacetic acid, m-sulphobenzoic acid, p-sulphobenzoic acid, benzoic acid-(1)-disulphonic acid-(3:5), 2 - chloro - benzoic acid - (1) - sulphonic acid-(4), 2 - hydroxybenzoic acid - (1) - sulphonic acid-(5), naphthol - (1) - sulphonic acid-(2), naphthol - (1)-disulphonic acid-(2,4), -(3,7), -(2,5) or -(3,6), 8 - chloronaphthol - (1) - disulphonic acid-(3,6), naphthol - (1) - trisulphonic acid-(2,4,8) and -(3,6,8), naphthol - (2) - sulphonic acid-(1), naphthol - (2) - trisulphonic acid-(3,6,8), 1:7 - dihydroxy - naphthalene sulphonic acid-(3), 1:8 - dihydroxy - naphthalene disulphonic acid-(2:4), chromotropic acid, 2-hydroxynaphthoic acid - (3) - sulphonic acid-(6) and 2 - hydroxycarbazole - sulphonic acid-(7);
5. Aminosulphonic acids: Amidosulphonic acid, hydroxylamine - monosulphonic acid, hydrazine - disulphonic acid, sulphanilic acid, N - phenylaminomethanesulphonic acid, 4:6 - dichloroaniline - sulphonic acid-(2), phenylenediamine - (1:3)-disulphonic acid-(4:6), N - acetylnaphthylamine - (1) - sulphonic acid-(3), naphthylamine - (1) - sulphonic acid-(2), naphthylamine - (2) - sulphonic acid-(1) or (5), naphthylamine - (2) - disulphonic acid-(3,7), -(3,6), -(4,7), -(4,8) or -(5,7), naphthylamine - (2)-trisulphonic acid-(3,6,8) or -(4,6,8), 4:4' - di-(p - aminobenzoylamino) - diphenylurea - disulphonic acid 3:3' phenylhydrazine - disulphonic acid-(2:5), 2:3 - dimethyl - 4-amino - azobenzene - disulphonic acid-(4':5), 4' - aminostilbene - disulphonic acid - (2:2') - (4 - azo - 4) - anisole, carbazole - disulphonic acid-(2:7), taurine, N - methyl - taurine, N-butyltaurine, 3 - amino - benzoic acid - (1)-sulphonic acid-(5), 3 - amino - toluene - N-methane - sulphonic acid, 6 - nitro - 1:3-dimethylbenzene - 4 - sulphamic acid, 4:6-diaminobenzene - disulphonic acid-(1:3), 2:4-diamino - toluene - sulphonic acid-(5), 4:4'-diaminodiphenyl - disulphonic acid-(2,2'), 2-aminophenol - sulphonic acid - (4), 4:4'-diamino - diphenylether - sulphonic acid-(2), 2 - aminoanisole - N - methanesulphonic acid, 2 - amino - diphenylamine - sulphonic acid, and 2:4 diaminobenzene-sulphonic acid;
6. Organic phosphorus compounds such as derivatives of phosphinic acid, phosphonous acids, phosphonic acid and phosphoric acids and esters of phosphorous and of phosphoric acid and their thionanalogues, e.g. bis - ( $\alpha$ -hydroxyisopropyl) - phosphinic acid, hydroxy-alkanephosphonic acids, phosphorous acid-bis - glycollic ester, phosphorous acid - bis-propylene glycol ester, phosphoric acid, phosphoric acid - bis - glycollic ester and phosphoric acid - bis - propylene glycollic ester;
7. The hydroxy, mercapto- and amino-carboxylic and -sulphonic acids, polycarboxylic and polysulphonic acids also include the addition products (which may be saponified) of unsaturated acids such as acrylic acid, methacrylic acid and unsaturated nitriles such as acrylonitrile, of cyclic dicarboxylic acid anhydrides such as maleic acid, phthalic acid and succinic acid anhydride, of sulphocarboxylic acid anhydrides such as sulphoacetic acid-, o-sulphobenzoic acid anhydride, of lactones such as  $\beta$ -propiolactone,  $\gamma$ -butyrolactone, the addition products of reaction products of olefines with sulphur trioxide such as carbyl sulphate, of epoxycarboxylic and epoxysul-

phonic acids such as glycidic acid, 2:3-epoxy-propane-sulphonic acid, of sultones such as 1:3 - propanesultone, 1:4 - butanesultone, 1:8 - naphthosultone, of disulphonic acid anhydrides such as benzene-(1:2)-disulphonic acid anhydride to aliphatic and aromatic amines such as ethylene - 1:2 - diamine, hexamethylene - 1:6 - diamine, isomeric phenylene diamines, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hydrazines which may be alkylated, ammonia, amino alcohols such as hydroxyalkylated amines and hydrazines such as ethanolamine, diethanolamine, triethanolamine, ethanol ethylene diamine, ethanol hydrazine, alcohols such as ethylene glycol, propylene glycol, butane-1:3-diol and butane-1:4-diol, hexane-1:6-diol, polyhydric alcohols such as trimethylol-propane, glycerol, hexanetriol, addition products, which may be hydrogenated, of epoxy compounds and ethylene imine compounds, such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide, ethylene imine and unsaturated nitriles such as acrylonitrile to aliphatic and aromatic aminocarboxylic acids and aminosulphonic acids, the reaction products of hydroxyalkane sulphonic acids, halogen carboxylic acids and halogen sulphonic acids with hydrazines which may be alkylated, such as hydrazinoacetic acid, hydrazinoethane sulphonic acid, hydrazinomethanesulphonic acid, the saponified addition products of cyanohydrines to hydrazines, such as 1:2-hydrazino-bis-isobutyric acid and the addition products of sodium hydrogen sulphite to olefinically unsaturated compounds such as allyl alcohol, maleic acid, -bis-ethylene- and -bis-propylene-glycol, ester of maleic acid;

40 8. Hydrazinocarboxylic acids such as hydrazinodicarboxylic acids.

Compounds suitable for converting the above compounds 1 to 8 into the salt form include the following:

- 45 1. Organic bases such as monofunctional primary, secondary and tertiary amines, e.g. methylamine, diethylamine, triethylamine, trimethylamine, dimethylamine, ethylamine, tributylamine, pyridine, aniline and toluidine,
- 50 alkoxyated amines such as ethanolamine, diethanolamine, triethanolamine, methyl diethanolamine and oleyldiethanolamine; polyfunctional polyamines in which the individual amino groups may differ in their basicity, e.g.
- 55 polyamines obtained by hydrogenation of addition products of acrylonitrile to primary and secondary amines, per- or partially alkylated polyamines such as N:N-dimethylethylenediamine; compounds such as  $\alpha$ -amino pyridine and N:N-dimethylhydrazine;
- 60 2. Inorganic bases, compounds which are basic in reaction or which split off bases, such as ammonia, monovalent metal hydroxides, -carbonates and -oxides such as sodium
- 65 hydroxide, potassium hydroxide.

The preparation of the anionic polyurethanes is carried out in known manner with or without solvents. In general, a prepolymer is first prepared from the higher molecular weight compound, for example the polyhydroxy compound, and the polyisocyanate, with or without solvent, at 80 to 150°C, and this prepolymer is then further reacted at 20 to 150°C, and if desired in solution, with chain lengthening agents, if employed, and with compounds having at least one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation, which compounds may if desired be dissolved in an organic solvent or in water. Where compounds having groups capable of salt formation are employed, the resulting polyurethane is subsequently converted at least partly into the salt form in known manner with the use of organic or inorganic bases by adding these in an organic or inorganic solvent, or without a solvent, at temperatures between 20 and 150°C. Their quantity depends on the amount of anionic groups present in the polyurethanes. The addition of an excess thereof is only suitable if they are volatile compounds which are easily removed. It is frequently advantageous to use less than equivalent amount of neutralising agent in order to obtain a certain degree of hydrophobicity and adjust the pH to a certain value. Bi- and polyfunctional neutralising agents such as polyamines are preferably used in excess in order to suppress a bilateral reaction which would cause chain lengthening or cross-linkage. Compounds in which the individual groups differ in their basicity may be used. It is also possible to add the salt forming component together with its salt-forming counterpart so that the salt is produced in situ.

If desired, the polyhydroxy compounds, chain lengthening agents and compounds having at least one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation may previously be mixed together. The reaction can be carried out in the presence of catalysts such as tertiary amines and/or organo-metallic compounds. The molar ratio of isocyanate groups to reactive hydrogen atoms is generally from 0.8:1 to 1.6:1. A ratio greater than 1.3:1 would generally only be of interest if it is desired to obtain an additional chemical cross-linking via biuret or allophanate groups.

To achieve a sufficient amount of salt-type groups in the products of the process, the proportion by weight of the salt-type groups incorporated should be more than 1% and not more than 15% (in the case of carboxylate group 8%), the expression "salt-type group" being used to denote e.g. the following groups:



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5 The cross-linking due to the presence of the salt-type groups manifests itself by the fact that the products of the process have dimensional stability when stored in water or in acetone whereas when stored in mixtures of tetrahydrofuran and water, composed of 9 parts by volume of tetrahydrofuran and 1 part by volume of water they lose their shape and largely dissolve. Acetone may also be used instead of tetrahydrofuran.

10 In the case of polyurethanes which in addition contain tertiary amino groups, the carboxylic acid and sulphonic acid groups introduced by the incorporation of compounds having at least one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation can be converted into their salt form by reaction with the basic tertiary nitrogen atoms contained in the polyurethane composition to achieve additional cross-linking effects which result in greater strength and elasticity of the products. If compounds are used which have only one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation, it is frequently advantageous to include a tri- or oligo functional component such as trimethylolpropane, water or diethylene triamine in order to compensate for the chain breaking effect of the compounds having only one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation.

35 The anionic polyurethanes described may be worked up according to the invention in a forming process to form, for example, foils, coatings, adhesifying agents and foam plastics. The production of the polyurethanes can be carried out without solvent in the melt or on rubber mixing rollers or in internal mixers and the composition can subsequently be formed in the desired manner. It can also be dissolved in a polar or a non-polar organic solvent which may contain water. If desired, the preparation of the polyurethanes may from the start be carried out in an organic solvent or an organic solvent may be introduced at an intermediate stage. The organic solvent may be aqueous insofar as when the solvent is added, the polyurethanes only contain sufficient isocyanate groups to react with the components containing reactive hydrogen atoms, which components may be already present or added at the same time, so that the isocyanate groups will be used up in this reaction before they can undergo an undesired reaction with water.

60 Conversion of the anionic polyurethane into the aqueous phase may be effected, for example, by partially or completely replacing the organic solvent after termination of the reaction and, if desired, salt formation. It is also possible to inject the dissolved or liquid

polyurethane free from solvent into water through nozzles, if desired under pressure. Ultrasonics may be employed to achieve a suitable state of subdivision in the aqueous phase. Polyurethanes having groups capable of salt-formation which must at least partly be converted into the salt form may, for example, be introduced into the aqueous solution of the complementary salt forming component with vigorous mechanical stirring. The organic solvent may be removed at the same time or at a later stage, if desired in vacuo. If the compound to be used according to the invention, which has at least one hydrogen atom reactive with isocyanate groups and at least one salt-type group or group capable of salt formation reacts more rapidly with isocyanates than with water then it may be added in aqueous solution to the not yet finished polyurethane composition which contains NCO groups, in which case the anionic polyurethane will be produced in the aqueous-organic phase. Again, in this case, the organic solvent may subsequently be removed.

90 Care should be taken in the choice of solvent to ensure that no solvent which reacts with isocyanate groups under the conditions of the reaction will be used in the preparation of the polyurethane. In the process according to the invention, any solvent which will not enter into reaction with the polyurethane or the organic and inorganic bases may be used. Preferred solvents are hydrocarbons which may be halogenated, ketones, alcohols, esters and nitriles, e.g. acetone, methyl ethyl ketone, isopropanol, tertiary butanol, acetonitrile, ethanol, methanol, ethyl acetate, methylene chloride, chloroform and carbon tetrachloride. High boiling solvents such as N,N-dimethylformamide and dimethylsulphoxide may also be used. The solvents may also contain water and in some cases water may be the major portion. Water may be used as solvent for the organic and inorganic bases used as counter components, if desired without the addition of organic solvents.

110 The aqueous solutions and dispersions obtained are stable without the addition of emulsifier but suitable anionic or neutral emulsifiers and dispersing agents may be added, e.g. casein hydrolysed with ammonia, fatty alcohol sulphonates, polyvinyl alcohol, hydroxyethylated phenols, oleyl alcohol polyglycol ether or natural products such as gelatine, gum arabic, tragacanth, fish glue, agar agar and salts of resinic acids.

115 The dispersions may be blended with dispersions of the same charge, e.g. with polyvinyl chloride- polyethylene-, polystyrene-, polybutadiene- and copolymer resin dispersions.

120 Finally, fillers, plasticisers, pigments, hydrofluoric acid and silicic acid sols, aluminium,

clay dispersions and asbestos dispersions may be incorporated into the dispersions.

The solutions or dispersions of the anionic polyurethane in organic or aqueous-organic solvents or water are stable and can be stored and transported and can be worked up in a forming process whenever desired at a later date. In general they dry directly to form dimensionally stable synthetic resin coatings but the forming of the products may also be carried out in the presence of cross-linking agents known per se. For this purpose, polyfunctional, cross-linking substances are added to the polyurethane compositions in the course of the process and cause chemical cross-linking after evaporation of solvent, if present, at room or elevated temperature. Examples of such agents are sulphur, sulphur soils, formaldehyde and substances which give off formaldehyde or react like formaldehyde, free and partially or completely masked polyisocyanates, carbodiimides, polyamines, compounds of divalent and polyvalent metals such as oxides, carbonates hydroxides of calcium, zinc, magnesium, which are preferably used in less than equivalent quantities in relation to the carboxylic acid and sulphonic acid groups in the polyurethane in order to achieve cross-linking, organic and inorganic peroxides. The cross-linking agents, fillers, pigments, blending agents and other additives, which may be dissolved or in suspension, may be added in the course of the process of the polyurethanes which may be dissolved or dispersed in an organic solvent or in water, or they may be incorporated on mixing rollers.

The possibility of employing polyurethane masses of very different compositions in a form suitable for application provides many new possibilities of application. Thus they can be used for the production of articles by the dip moulding process, for the production of foam plastics by the latex churning process, and by addition of electrolyte to the aqueous solutions and dispersions they can give rise to coagulates which can be worked up on mixing rollers like the solvent-free polyurethane compositions, and by evaporation of any solvent present it is possible to obtain non-sticky or sticky films and foils and crystalline powders. The products of the process are suitable for use as coatings and for impregnating woven and non-woven textiles, leather, paper, wood and metals and as antistatic and crease-resistant finishes and as binders for fleeces, adhesives, adhesifying agents, backing agents, hydrophobic agents, plasticisers, binders, e.g. for cork powder or wood flour, glass fibres, asbestos, paper type materials, plastics- or rubber waste and ceramic materials, as auxiliary agents in calico printing and in the paper industry, as additives to polymer dispersions and as sizes and as finishes for leather.

The following Examples illustrate the invention:—

#### EXAMPLE 1

250 g. of adipic acid-ethylene glycol polyester (OH number 56) were dehydrated in vacuo at 120°C. and then treated with 46.9 g. of 4:4'-diphenylmethane diisocyanate at 80°C. The melt was kept at 80°C. for 30 minutes and stirred during this time and then cooled to 55°C. and 7.8 g. of 2:4-diaminobenzene sulphonic acid in 50 ml. of water were then added. The reaction product was diluted with 585 ml. of acetone. a) 200 g. of the reaction mixture were further diluted with 200 ml of acetone and neutralised at 50°C. with 1.5 g. of triethanolamine. After introducing 137 ml of water dropwise, the acetone was distilled off. A dispersion remained behind which, after evaporation of the water, formed a solid, nonsticky elastic film. b) 80 g. of the reaction mixture were diluted with 200 ml of acetone. After the addition of 0.2 g. of triethylenediamine in 50 ml. of acetone at 50°C., 54 ml of water were added dropwise and the acetone distilled off. The dispersion obtained dried to a firm film.

#### EXAMPLE 2

271 g. of a polyester of adipic acid and ethylene glycol (OH number 51.8) were dehydrated for ½ hour at 120°C. and cooled to 80°C. and then reacted with 62.5 g. of 4:4'-diphenylmethane diisocyanate. A solution of 51.1 g. of potassium 4:4'-diaminodiphenyldihydroxyacetate in 100 ml. of water was added at 55°C. After the addition of 820 ml. of acetone, the mixture was stirred for another ½ hour.

204 g. of water were added dropwise at 55°C. to 300 g. of the reaction mixture and the acetone was removed in vacuo. The latex obtained formed a hydrophobic film of good tensile strength, which softened in water and swelled in acetone without dissolving and without losing its shape. Almost complete solution took place, however, in aqueous acetone, consisting of 9 parts by volume of acetone and 1 part volume of water.

#### EXAMPLE 3

271 g. of a polyester of adipic acid and ethylene glycol (OH number 51.8) were dehydrated for ½ hour at 120°C. and 12 mm Hg and then reacted at 80°C. with 67.1 g. of 4:4'-diphenylmethane diisocyanate. 18.8 g. of tartaric acid in 350 ml. of acetone were reacted with the prepolymer at 55°C., and 100 ml. of acetone were then added. a) 200 g. of the reaction mixture were dissolved in 200 ml. of acetone at 50°C., treated with 7.1 g. of triethylamine and 200 ml of water were added dropwise. After removing the acetone by evaporation, a dispersion was obtained which had good film forming properties. The films had good tensile strength.

- b) The process was carried out as under a) except that 10.4 g. of triethanolamine were added instead of 7.1 g. of triethylamine. The dispersion obtained formed somewhat more hydrophilic films than those obtained under a).

#### EXAMPLE 4

- 218.5 g of a polyester of adipic acid, neopentyl glycol and hexanediol (OH number 63) were dewatered in vacuo at 120°C. for 30 minutes. After addition of 47.0 g. of 1:6-hexamethylene diisocyanate, the melt was stirred for 2 hours at 120°C. and then cooled to 60°C. 18.75 g. of tartaric acid were dissolved in 450 ml. of acetone and added to the melt. 12.8 g. of triethylamine in 100 ml. of acetone were added immediately afterwards. After the reaction was complete, and after addition of 18.6 g. of triethanolamine in 100 ml of acetone, 630 ml of water were added dropwise and the acetone was removed by evaporation. The dispersion remaining behind dried to form elastic films.

#### EXAMPLE 5

- 271 g. of a polyester of adipic acid and ethylene glycol (OH number 51.8) were dewatered at 120°C. and then reacted with 176.8 g. of 4:4'-diphenylmethane diisocyanate at 80°C. and with 107.9 g. of citric acid in 375 ml. of acetone at 55°C. At the same time, a further 831 ml of acetone were added. The reaction product formed a yellow gelatinous mass.

- 200 g. of the reaction mixture were diluted with 100 ml. of acetone, 11.2 g. of triethanolamine were added and 184 ml. of water were introduced dropwise into the solution. After distilling off the acetone, a yellow dispersion was obtained which dried to a powder.

#### EXAMPLE 6

- A prepolymer obtained from 271 g. of a polyester of adipic acid and ethylene glycol (OH number 51.8) and 225 g. of 4:4'-diphenylmethane diisocyanate was diluted with 1000 ml of acetone at 55°C. and reacted with 144 g. of citric acid in 500 ml. of acetone.

- 200 g. of the reaction mixture were dissolved in 100 ml. of acetone and treated with 3.8 g. of triethylamine and 2.3 g. of triethylene diamine in 50 ml. of acetone at 55°C. After the dropwise addition of 240 ml of water and removal of the acetone, a creamy dispersion was obtained which formed a turbid film.

#### EXAMPLE 7

- 116.9 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 59.8) were dewatered for 2 hours at 120°C. and then reacted with 136.5 g. of hexane-1:6-diisocyanate. The prepolymer obtained was treated with a solution of 73.5

g. of crystallised orthophosphoric acid and 75.8 g. of triethylamine in 450 ml. of acetone-trile at 55°C. and the components reacted together, carbon dioxide being liberated. After the addition of 264 ml of acetone and 600 ml. of water, the organic solvents were removed in vacuo. The paste obtained dried to a very fine crystalline powder having a melting point of 270 to 280°C. The product did not dissolve in water.

#### EXAMPLE 8

218 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) were dewatered at 120°C. and 12 mm Hg and then reacted with 39 g. of hexane-1:6-diisocyanate. After 2 hours at 120°C., the reaction mixture was cooled, the melt was diluted with 330 ml. of acetone at 55°C. and 92 ml. of an aqueous 20% sodium taurine solution were then added. After the dropwise addition of 55 ml. of water and distilling off the acetone, a 30% latex was obtained which dried to high tensile, elastic and transparent films. The films were dimensionally stable when stored in water and acetone but dissolved when they were stored in mixtures of acetone and water consisting of 9 parts by volume of acetone and 1 part by volume of water.

The foils obtained by the following mechanical properties:

|                       |                       |
|-----------------------|-----------------------|
| Tensile strength      | 55 kg/cm <sup>2</sup> |
| Tension at 100%       | 49 kg/cm <sup>2</sup> |
| Elongation at tearing | 198%                  |
| Tear resistance       | 6.2 kg/cm.            |

#### EXAMPLE 9

A prepolymer obtained from 218.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) and 32.6 g. of hexane-1:6-diisocyanate was dissolved in 330 ml. of acetone at 55°C. and added dropwise into 46 g. of a prepared aqueous 20% sodium taurine solution which was vigorously agitated at the same time. When the reaction was complete 560 ml. of water were added and the acetone removed by evaporation. The latex obtained had a concentration of 31% and forms elastic, high tensile films which were not soluble in acetone or in water but dissolved in aqueous acetone.

The material had the following mechanical properties:

|  |                       |
|--|-----------------------|
| Tensile strength                             | 57 kg/cm <sup>2</sup> |
| Tension at 100%                              | 24 kg/cm <sup>2</sup> |
| Tension at 500%                              | 54 kg/cm <sup>2</sup> |
| Elongation at tear                           | 579%                  |
| Permanent elongation at break after 1 minute | 2%                    |
| Tear resistance                              | 11 kg/cm.             |

#### EXAMPLE 10

212.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number



65.9) were dewatered at 120°C. and then reacted with 51.6 g. of 4:4'-diphenylmethane diisocyanate at 80°C. for 30 minutes. The prepolymer was taken up in 365 ml. of acetone at 55°C and treated with 61.2 g. of an aqueous 20% sodium taurine solution. After addition of 474 ml. of water and distilling off the acetone, a 38.7% slightly opaque dispersion was obtained. After evaporating off the solvent, elastic, transparent foils were obtained which were soluble in aqueous acetone but not in acetone or water.

#### EXAMPLE 11

The prepolymer was prepared by stirring together 218.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) and 30.6 g. of hexane-1:6-diisocyanate for 2 hours at 120°C. After cooling, the melt was taken up in acetone and treated with 32.2 g. of an aqueous 20% sodium taurine solution. After the addition of 320 ml. of water and distilling off the acetone, a latex was obtained which had a solids content of 39% and pH 6 to 7. The latex formed clear, transparent films of high tensile strength and elasticity. The sodium polyurethane sulphonate having an SO<sub>3</sub> content of 1.37% was soluble in aqueous acetone without leaving a residue but in acetone and water it only swelled slightly and maintained its shape.

The material had the following mechanical properties:

|  |                       |
|--|-----------------------|
| Tensile strength                             | 73 kg/cm <sup>2</sup> |
| Tension at 100%                              | 19 kg/cm <sup>2</sup> |
| Tension at 500%                              | 55 kg/cm <sup>2</sup> |
| Elongation at tear                           | 716%                  |
| Permanent elongation at break after 1 minute | 1%                    |
| Tear resistance                              | 15 kg/cm              |

#### EXAMPLE 12

A prepolymer prepared from 218.5 g. of a polyester of adipic acid 1,6-hexandiol and neopentyl glycol (OH number 63) and 37 g. of hexane-1:6-diisocyanate was diluted with 350 ml. of acetone and treated with 67.1 g. of an aqueous 30% sodium N-methyltaurine solution. A 36% latex was obtained after the addition of 500 ml of water and removal of the acetone by evaporation.

#### EXAMPLE 13

218.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) were dewatered in vacuo at 120°C., treated with 52 g. of neopentyl glycol and 53 g. of diethylene glycol and reacted with 258 g. of hexane-1:6-diisocyanate at 60°C. The melt was heated and left at 120°C. for 2 hours, taken up in 584 ml. of acetone, and after the addition of 184 g. of a 20% aqueous sodium taurine solution, 750 ml of water were added dropwise. After distilling off the ace-

tone, a 41% latex was obtained. The SO<sub>3</sub> content of the polyurethane was 3.24%. The foils obtained were opaque, hard and of very high tensile strength.

#### EXAMPLE 14

A prepolymer obtained from 218.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) and 55 g. of hexane-1:6-diisocyanate was taken up in 1 litre of acetone (water content 0.18%) and a mixture of 7.5 g. of ethylene diamine, 15.3 g. of 1:3-propanesultone and 12.6 g. of triethylamine in 50 ml. of water was added at 55°C. After the addition of 550 ml. of water, the acetone was removed in vacuo. A 36.6% colloidal solution which had a pH value of 6 was obtained. The films remaining behind after drying of the colloidal solution were of extraordinarily high tensile strength and elastic

#### EXAMPLE 15

The process was carried out as in Example 14 except that the acetone solution of the prepolymer was reacted with a mixture of 7.5 g of ethylene diamine, 15.3 g. of 1:3-propane-sultone and 70 ml. of a 10% potassium hydroxide solution in 50 ml. of water. After the addition of 480 ml. of water and removal of the acetone by evaporation, a 36.8% latex was obtained which had a pH value of 6 to 7. The foils obtained from this were highly elastic, transparent and resistant to boiling water.

The physical properties of the foils were:

|  |                        |
|--|------------------------|
| Tensile strength                             | 284 kg/cm <sup>2</sup> |
| Tension at 100%                              | 47 kg/cm <sup>2</sup>  |
| Tension at 500%                              | 146 kg/cm <sup>2</sup> |
| Elongation at tearing                        | 594%                   |
| Permanent elongation at break after 1 minute | 35%                    |
| Tear resistance                              | 24 kg/cm.              |

#### EXAMPLE 16

218.5 g. of a polyester of adipic acid, 1,6-hexanediol and neopentyl glycol (OH number 63) were dewatered at 120°C. and 12 mm Hg for 30 minutes and reacted with 84.2 g. of hexane-1:6-diisocyanate at 120°C. in 2 hours. The melt was dissolved in 700 ml. of acetone at 55°C. and reacted with 368 g. of a 20% aqueous sodium taurine solution. After the dropwise addition of 1100 ml. of water and distilling off the acetone, 1657 g. of a viscous gelatinous, acetone-free 22.7% latex was obtained which dried to turbid films which could be powdered. The product melted between 250 and 270°. The product swelled in water without loss of shape and dissolved on heating to a turbid colloidal solution. It was partially soluble in a mixture of 9 parts of acetone and 1 part of water even in the cold.



## EXAMPLE 17

212.5 g. of an adipic acid-1,6-hexane diol-neopentyl-glycol-polyester (OH number 65.85) were reacted at 120°C. with 51 g. of 1,6-hexane diisocyanate. The adduct was dissolved at 55° in 800 ml of acetone. An aqueous solution of 18.25 g. of lysine and 70 ml. of 10 per cent potassium hydroxide solution in 50 ml of water were added to the solution of the adduct. When the reaction was complete, 450 ml of water were added and acetone was distilled off. A stable dispersion was obtained with an pH-value of 8 and a solid content of 41 per cent. The dispersion after drying yielded clear, elastic, high tensile strength foils.

## EXAMPLE 18

An adduct of 420 g. of an adipic acid-1,6-hexane diol-neopentylglycol polyester (OH number 65.85) and 65.2 g. of hexane diisocyanate were dissolved in 1000 ml of acetone. A solution of 9.4 g. of glycol and 50 ml of sodium hydroxide solution in 100 ml of water were added thereto. After addition of 900 ml of water acetone was distilled off. A dispersion was obtained with a solid content of 30.9 per cent.

## EXAMPLE 19

250 g. of a polypropylene glycol ether (OH number 56) were reacted at 120°C. for two hours with 126.2 g. of toluylene diisocyanate (2,4- and 2,6-isomers 65:35). After cooling to 70°C. the reaction mixture had added thereto 52 g of neopentyl glycol in 100 ml of acetone. The mixture was held for five hours at 60°C. 800 ml of acetone were then added. After addition of a mixture of 50 ml of water, 3.76 g of ethylene diamine, 7.63 g of 1,3-propane sultone and 25 ml of 10 per cent aqueous sodium hydroxide solution 450 ml of water are stirred into the mixture. After distilling off acetone a stable dispersion was obtained with a solid content of 47 per cent. The residual content of acetone in the dispersion was determined by gas chromatography or by conversion into the oxime. It was found as 0.05 to 1 per cent depending on the course of distillation.

## EXAMPLE 20

An adduct was prepared at 120° from 106.3 g of an adipic acid-1,6-hexane diol-neopentyl-glycol-polyester (OH number 65) and 289.0 g of 1,6-hexane diisocyanate at 60°C. with 78.0 g of neopentyl glycol and 79.5 g of diethylene glycol in 100 ml of acetone were added and then the mixture was held for eight hours at 60°C. 1000 ml of acetone were added and then a mixture of 50 ml of water, 7.52 g of ethylene diamine, 15.25 g of 1,3-propane sultone and 70 ml of 10 per cent aqueous potassium hydroxide solution. When the reaction was complete 1100 ml of water

were stirred into the mixture and acetone was distilled off. A stable 40 per cent dispersion was obtained with a pH value of 6. The remaining dispersion after drying at 120°C. was lustrous, clear, light-stable and water-resistant.

## EXAMPLE 21

210 g of an adipic acid-1,6-hexane diol-neopentylglycol-polyester (OH number 66.6) were reacted together for 30 minutes at 80°C. with 48.5 g of 4,4'-diphenylmethane diisocyanate. 800 ml of acetone were added to the melt and reacted at 55 to 60°C. with 8.2 g of glycooll potassium in 80 ml of water. Finally 500 ml of water were added. The acetone was distilled off. A 33.8 per cent dispersion is obtained.

## EXAMPLE 22

250 g. of polypropylene glycol ether (OH number 56) were reacted with 38 g of 1,6-hexane diisocyanate at 130°C. 800 ml of acetone were added at 60°C. After reaction of the adduct solution with a mixture of 3.76 g of ethylene diamine, 7.63 g of 1,3-propane sultone and 25 ml of 10 per cent aqueous sodium hydroxide in 50 ml of water 550 ml of water were added and the acetone was distilled off. The dispersion thus obtained had a solid content of 32.0 per cent with a pH-value of 6. It was precipitated by a hot 5 per cent aqueous calcium chloride solution. It was however stable to concentrated ammonia solution. The films remaining behind after drying of the dispersion were soft, flexible and elastic.

## EXAMPLE 23

263 g. of poly-1,4-tetramethylene-glycol-ether (OH number 63.3) were reacted at 120°C. for two hours with 38.0 g of 1,6-hexane diisocyanate. The adduct was dissolved in 700 ml of acetone. A mixture of 3.76 g of ethylene diamine, 7.63 g of 1,3-propane sultone and 35 ml of 10 per cent aqueous potassium hydroxide solution in 50 ml of water were added. After addition of 425 ml of water the acetone was distilled off. A 42 per cent dispersion was obtained.

## EXAMPLE 24

350 g of a polyester of adipic acid and diethylene glycol prepared by polycondensation (OH number 10.0: molecular weight 11,200) were dehydrated by heating for 30 minutes at 120°C/20 mm Hg pressure, and then reacted over a period of two hours at 120°C. with 20 g of 1,6-hexane diisocyanate. The highly viscous melt was cooled, taken up with 900 ml of acetone and mixed at 55°C. with an aqueous solution of 14.9 g of potassium ethylene diamine-N-propane sulphonate in 85 ml of water. On completion of the reaction, 600 ml of water are added, and the

acetone distilled off in vacuo at 55 to 60°C. 920 g of a stable emulsifier-free dispersion with a pH-value of 6 being obtained. The dispersion dried at room temperature to form  
 5 a soft elastic and slightly tacky film.

#### EXAMPLE 25

Following 30 minutes dehydration at 120°C in vacuo, 700 g of adipic acid diethylene glycol polyester (OH number 10) were reacted for 2 hours at 110°C. with 45.6 g of  
 10 toluylene diisocyanate (2,4 and 2,6-isomers in ratio of 65:35). The melt was taken up with 1400 ml of acetone and mixed at 55°C. with 27.8 g of sodium ethylene diamine-N-  
 15 propane sulphonate in 170 ml of water. Stirring was continued at 55°C. Following the addition of 1200 ml of water, the acetone was distilled off in vacuo at 55°C. A 39.2% dispersion was formed which remained stable  
 20 without the addition of an emulsifier and from which clear, elastic and soft films were obtained by removing the solvent. The dispersion was precipitated by the addition of 2% hot magnesium sulphate solution, although it  
 25 is compatible with a concentrated, aqueous solution of ammonia.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of polyurethane resins which comprises reacting together a predominantly linear compound having  
 30 reactive hydrogen atoms and at least one hydroxyl group and a molecular weight of 300 to 20,000, a polyisocyanate, if desired chain lengthening agents having reactive  
 35 hydrogen atoms, and a compound having at least one hydrogen atom reactive with isocyanate groups and at least one anionic salt-type group or group capable of anionic salt formation, the ratio of isocyanate groups to  
 40 hydrogen atoms reactive with isocyanate groups in the compounds capable of salt formation being such that the groups capable of salt formation present do not undergo reaction with the isocyanate groups, and the  
 45 resulting polyurethane is subsequently converted at least partly to the salt form by reaction with an organic or inorganic base in the case where groups capable of salt formation are present, the proportion by weight of the  
 50 salt type groups contained in the polyurethane being more than 1% and not more than 15% and, when the groups capable of salt forma-

tion are carboxyl groups, not more than 8%.

2. A process as claimed in claim 1 in which the polyisocyanate is a masked polyisocyanate, an isocyanate which has been partially reacted. 55

3. A process as claimed in claim 1 or claim 2 in which the chain-lengthening agent is water. 60

4. A process as claimed in any one of claims 1 to 3 in which the predominantly linear compound containing at least one hydroxyl group is reacted with the polyisocyanate at from 80 to 150°C, and the pre-polymer so formed is further reacted at 20 to 150°C. with a chain-lengthening agent, if employed and with the compounds having at least one hydrogen atom reactive with isocyanate groups and at least one salt type group or group capable of salt formation. 65

5. A process as claimed in any one of claims 1 to 4 in which the molar ratio of isocyanate group to reactive hydrogen atoms is from 0.8:1 to 1.6:1. 70

6. A process as claimed in any one of claims 1 to 5 in which the preparation is carried out in an organic solvent and water is added when conversion to the salt form is effected and the organic solvent is then removed and finally the water is removed while a shape is imparted to the product. 75

7. A process as claimed in claim 6 in which after salt formation, the organic solvent with water is partly or completely replaced by water and the aqueous solvent is finally removed and at the same time shape is imparted to the product. 80

8. A process as claimed in any of claims 1 to 7 in which the shaping of the product is carried out in the presence of cross-linking agents. 85

9. A process for the preparation of polyurethane resins substantially as herein described with reference to any one of the Examples. 90

10. Polyurethane resins when produced by a process as claimed in any of claims 1 to 9. 95

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